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IS 12479 (1988): Methods for analysis of solvent systems used for removal of water formed deposits [CHD 13: Water Quality for Industrial Purposes]

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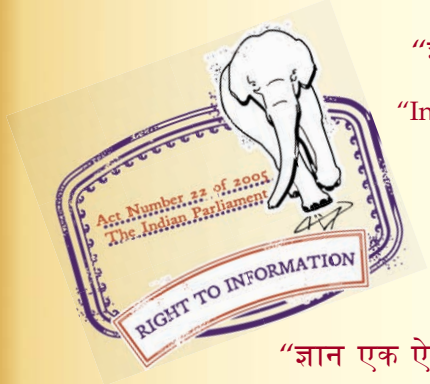

"ज्ञान एक ऐसा खजाना है जो कभी चुराया नहीं जा सकता है"
Bhartṛhari—Nītiśatakam
"Knowledge is such a treasure which cannot be stolen"

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IS : 12479 - 1988
(Reaffirmed 2003)

Indian Standard

METHODS FOR ANALYSIS OF SOLVENT SYSTEMS USED FOR THE REMOVAL OF WATER FORMED DEPOSITS

UDC 66·061 : 66·074·3

BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

Gr 8 *May* 1989

Indian Standard

METHODS FOR ANALYSIS OF SOLVENT SYSTEMS USED FOR THE REMOVAL OF WATER FORMED DEPOSITS

0. FOREWORD

0.1 This Indian Standard was adopted by the Bureau of Indian Standards on 31 August 1988, after the draft finalized by the Boiler Water Sectional Committee had been approved by the Chemical Division Council.

0.2 These methods cover analysis of both the solvents and the deposits in the solvents used for the chemical cleaning of industrial equipment. Prior to analysis for soluble constituents in the solvent, the sample is filtered to remove insoluble matter.

0.3 The procedures prescribed in this standard cover methods for determination of concentration of the following solvents during or after use:

Acetic acid, ammonia, ammonium sulphate in ammonia, chromic acid, formic acid, hydrazine, hydrochloric acid, hydrochloric acid with copper complexing agents, hydroxy acetic acid and formic acid mixtures, phosphoric acid, potassium hydroxide, sodium or potassium bromate, sodium carbonate, sodium hydroxide, sodium phosphate, sulfamic acid and sulphuric acid.

0.4 In the preparation of this standard, considerable assistance has been derived from ASTM D-2790-1983 'Analysis of solvent systems used for removal of water formed deposits' published by the American Society for Testing and Materials, Philadelphia, USA, 1985.

0.5 In reporting the results of a test or anylysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960*.

*Rules for rounding off numerical values (*revised*).

1. SCOPE

1.1 This standard covers the analysis of both the solvents and the deposits, constituents in the solvents used for the chemical cleaning of industrial equipment.

2. TERMINOLOGY

2.1 For the purpose of this standard the definitions given in IS : 11671-1985* shall apply.

3. ACID CONTENT OF ACID SOLVENTS

3.1 Principle — The acid concentration is determined by titration with standard sodium hydroxide solution using a suitable indicator.

3.2 Interference — There is no interference when analyzed for original acid concentration of various acid solvents. Iron interferes when determining the concentration of acid remaining in the solvents after use as cleaning solutions. This can be minimized by the proper choice of acid-base indicators. It is significant only when the acidic solvent contains over 1 percent iron in solution.

*Glossary of terms relating to boiler water.

3.3 Reagents

3.3.1 *Chlorophenol Red Indicator Solution* — 0·5 g/l.

3.3.2 *Mixed Indicator Solution* — Dissolve 0·05 g of bromocresol green in 50 ml of rectified spirit and 0·75 g of methyl red in rectified spirit. Mix well these two solutions.

3.3.3 *Methyl Red Indicator* — 1 g/l.

3.3.4 *Phenolphthalein Indicator Solution* — 10 g/l.

3.3.5 *Standard Sodium Hydroxide Solution* — 0·5 N.

3.4 Procedure

3.4.1 Dilute an aliquot of the sample with water to 30 to 50 ml in a 125 ml Erlenmeyer flask. Choose the aliquot size so that a titration volume greater than 5 ml and less than 15 ml of 0·5 N sodium hydroxide solution is required. In case of concentrated acids, this may require diluting 5 to 10 ml of the sample to 50 or 100 ml before taking an aliquot for titration with 0·5 N sodium hydroxide solution.

3.4.2 Add 4 drops of the designated indicator solution and titrate with 0·5 N sodium hydroxide solution until the colour of the solution changes from red to yellow for methyl red, from yellow to red for chlorophenol red, from red through grey to blue-green for mixed indicator, and from colourless to red for phenolphthalein.

3.4.3 Select the appropriate indicator from Table 1.

3.4.4 Record the millilitres of sodium hydroxide solution required for the titration (*A*).

TABLE 1 SELECTION OF INDICATOR

Acid	Methyl Red (MR)	Chloro-phenol Red (CPR)	Mixed (Mix)	Phenol-phtha-lein (PE)
Acetic acid	*O*	—	*O-S*	—
Citric acid	—	—	—	*O*
Formic acid	*O*	*O-S*	*O-S*	—
Hydrochloric acid	*O*	—	*O-S*	—
Hydroxyacetic acid	*O*	*O-S*	*O-S*	—
Phosphoric acid	—	—	*O-S*	*O*
Sulfamic acid	*O*	—	*O-S*	—
Sulfuric acid	*O*	—	*O-S*	—
2-hydroxyacetic acid : 1 formic acid	*O*	*O-S*	—	—

O = Original concentration of acid solvent.
S = Spent solvents acid content.

3.5 Calculation

3.5.1 Calculate the concentration of the acid in the solvent in percent as follows:

Acetic acid, percent = $(AN/BS) \times 6{\cdot}0$

Citric acid, percent = $(AN/BS) \times 6{\cdot}4$

Formic acid, percent = $(AN/BS) \times 4{\cdot}6$

Hydrochloric acid, percent = $(AN/BS) \times 3{\cdot}6$

Phosphoric acid, percent = $(AN/BS) \times 7{\cdot}6$

Sulfamic acid, percent = $(AN/BS) \times 9{\cdot}8$

Sulphuric acid, percent = $(AN/BS) \times 4{\cdot}9$

2-hydroxyacetic acid : 1 formic acid, percent = $(AN/BS) \times 6{\cdot}6$

where

A = millilitres of sodium hydroxide solution required for the titration,

N = normality of sodium hydroxide solution,

B = millilitres of sample titrated, and

S = specific gravity of the sample.

3.5.2 If a dilution was required, multiply the answer by a dilution factor. For example, for 10 ml diluted to 100 ml prior to taking a 5 ml aliquot, the percent acid = $(AN/BS) \times 10 \times 6{\cdot}0$ for acetic acid.

4. INITIAL CITRIC ACID CONCENTRATION OF MONO AMMONIATED CITRIC ACID DURING FILLING

4.1 Principle — The citric acid concentration is determined by titration with a standard base. The citric acid concentration is calculated assuming a *p*H 4 solution or based on the quantity of the chemicals used.

4.2 Reagents

4.2.1 *Phenolphthalein Indicator Solution — See* **3.3.4.**

4.2.2 *Standard Sodium Hydroxide Solution* — 0·5 N.

4.3 Procedure

4.3.1 Pipette an aliquot of the sample containing 0·25 to 0·5 g of citric acid into a 50 ml Erlenmeyer flask. Add 10 to 20 ml of water, and 2 to 3 drops of phenolphthalein indicator. Titrate to a permanent pink colour with the standard base.

4.4 Calculation

4.4.1 Calculate the percent of citric acid as follows:

Citric acid, percent = $(ANF)/CS$

where

A = millilitres of sodium hydroxide solution required for the titration,

N = normality of sodium hydroxide solution,

F = 12·4 for *p*H 4 ammoniated citric acid solution. When the weight of citric acid and ammonia used to make up the *p*H 4 solution are known, then

$$F = \frac{19{\cdot}2}{\left[3 - \frac{\text{kg ammonia } (NH_3)}{\text{kg citric acid}} \times 11{\cdot}3\right]}$$

C = millilitres of sample titrated, and

S = specific gravity of the sample.

5. BROMATE OR PERSULPHATE IN AMMONIACAL SOLUTIONS

5.1 Principle — The bromate or persulphate in the solvent is reacted with potassium iodide (*KI*) and the liberated iodine is titrated with standard sodium thiosulphate ($Na_2S_2O_3$) solution using a starch indicator. Intensity of starch-iodine colour is increased by the endothermic hydration of potassium thiocyanate. In the case of a spent solvent, copper is first

determined as in **8** to **11** and the amount of $Na_2S_2O_3$ required for copper titration is deducted to obtain the bromate or persulphate content.

5.2 Reagents

5.2.1 *Hydrochloric Acid* — Mix one volume of concentrated acid (sp gr 1·19) with one volume of water.

5.2.2 *Potassium Iodide* — soild.

5.2.3 *Potassium Thiocyanate* — solid.

5.2.4 *Standard Sodium Thiosulphate Solution* — 0·1 N.

5.2.5 *Starch Indicator Solution*

5.3 Procedure

5.3.1 Dilute a 5 ml sample (C) with 30 to 50 ml of water in a 250-ml Erlenmeyer flask.

5.3.2 Add 5 ml of hydrochloric acid (1 + 1).

5.3.3 Add 5 g of potassium iodide to the sample, dissolve, stopper, and allow to stand for 5 min.

5.3.4 Titrate with 0·1 N sodium thiosulphate solution until almost colourless. Add starch indicator solution and continue the titration until nearly all of the purple colour disappears.

5.3.5 Add 2 g of potassium thiocynate and titrate to a colourless end point.

5.3.6 Record the millilitres of sodium thiosulphate solution required for the titration (A).

5.4 Calculation

5.4.1 Calculate the concentration of $NaBrO_3$ or $KBrO_3$ or $(NH_4)_2S_2O_8$ in the solvent in percent as follows:

$(NH_4)_2S_2O_8$, percent $= [(A - B) N \times 1{\cdot}14]/CS$

$KBrO_3$, percent $= [(A - B) N \times 2{\cdot}80]/CS$

$NaBrO_3$, percent $= [(A - B) N \times 2{\cdot}5]/CS$

where

A = millilitres of sodium thiosulphate ($Na_2S_2O_3$) solution required for copper plus bromate or persulphate titration,

B = millilitres of $Na_2S_2O_3$ solution required for titration of copper in the solvent (*see* **11**),

N = normality of $Na_2S_2O_3$ solution,

C = millilitres of sample titrated, and

S = specific gravity of the sample.

6. AMMONIA, POTASSIUM HYDROXIDE, SODIUM HYDROXIDE AND SODIUM CARBONATE IN CLEANING SOLUTIONS

6.1 Principle — The ammonia, potassium hydroxide (KOH), sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3) concentration is determined by titration with standard hydrochloric acid (HCl) using methyl orange indicator.

6.2 Interference

6.2.1 Sodium hydroxide and potassium permanganate ($KMnO_4$) are used as alkaline oxidizing treatment on organic deposits. The permanganate interferes with the determination of sodium hydroxide. This interference is eliminated by reacting permanganate with hydrogen peroxide (H_2O_2) and removing the precipitate by filtration.

6.3 Reagents

6.3.1 *Hydrochloric Acid* — 0·1 N.

6.3.2 *Hydrogen Peroxide* — 30 percent.

6.3.3 *Methyl Orange Indicator Solution* — 1 g per litre.

6.4 Procedure

6.4.1 Pipette an aliquot of the sample into an Erlenmeyer flask containing 25 to 50 ml of water. The aliquot volume should be chosen so that at least 5 ml, but not more than 15 ml of 0·1 N HCl is required for the titration.

6.4.2 For NaOH solutions containing permanganate, pretreat as follows:

6.4.2.1 Heat diluted sample to boil. Add hydrogen peroxide (30 percent) dropwise until the permanganate colour disappears and the manganese hydroxide [$Mn(OH)_3$] flocculates. Filter while hot through a highly retentive paper. Wash three times with water, collecting the filtrate and washings in a beaker, and proceed to **6.4.3.**

6.4.3 Add 3 drops of methyl orange indicator solution.

6.4.4 Titrate with 0·1 N hydrochloric acid to a red end point.

6.4.5 Record the millilitres of hydrochloric acid required for the titration (A).

6.5 Calculation

6.5.1 Calculate the concentration of ammonia, sodium carbonate, or alkali in the solvent or solution as follows:

Ammonia (NH_3), percent $= (AN/BS) \times 1{\cdot}7$

Potassium hydroxide (KOH), percent $= (AN/BS) \times 5{\cdot}6$

Sodium carbonate (Na_2CO_3), percent $= (AN/BS) \times 5{\cdot}3$

Sodium hydroxide (NaOH), percent $= (AN/BS) \times 4{\cdot}0$

where

A = millilitres of HCl required for the titration,

N = normality of HCl,

B = millilitres of sample titrated, and

S = specific gravity of the sample.

7. TRISODIUM PHOSPHATE AND SODIUM HYDROXIDE OR TRISODIUM AND DISODIUM PHOSPHATE IN NEUTRALIZING AND PASSIVATING SOLUTION

7.1 Principle — The trisodium phosphate (Na_3PO_4) is titrated to equivalence point of the first sodium in trisodium phosphate and the equivalence point of sodium hydroxide (NaOH) with hydrochloric acid (HCl) using phenolphthalein indicator. The titration is continued to the equivalence point of the second sodium in Na_3PO_4 using a mixed indicator. This method may be used to analyze solutions of Na_3PO_4 and disodium phosphate (Na_2HPO_4).

7.2 Reagents

7.2.1 *Hydrochloric Acid* — 0·05 N.

7.2.2 *Mixed Indicator* — *See* **3.3.2.**

7.2.3 *Phenolphthalein Indicator* — *See* **3.3.4.**

7.3 Procedure

7.3.1 Pipette 10 ml of filtered solvent into a 150 ml beaker.

7.3.2 Add 4 drops of phenolphthalein indicator solution and titrate with 0·05 N HCl until colourless. Record the volume (PE).

7.3.3 Add 4 drops of mixed indicator solution and continue titration without refilling the burette to a reddish-grey end point. Record the volume (ME).

7.4 Calculation

7.4.1 Calculate the percent of NaOH and Na_3PO_4 solutions as follows:

$$\text{Excess alkalinity as NaOH, percent} = [(2PE - ME) \times N \times 4]/AS$$

$$Na_3PO_4 \cdot 12H_2O, \text{ percent} = [(ME - PE) \times N \times 38]/AS$$

$$Na_3PO_4 \text{ (TSP), percent} = [(ME - PE) \times N \times 16{\cdot}4]/AS$$

7.4.2 Calculate the percent of Na_3PO_4 and Na_2HPO_4 solution as follows:

When $(2PE - ME) < 0$ or $ME > 2PE$, there is no excess NaOH; and

$$Na_3PO_4 \text{ (TSP), percent} = (PE \times N \times 16{\cdot}4)/AS$$

$$Na_2HPO_4 \text{ (DSP), percent} = [(ME - 2PE) \times N \times 14{\cdot}2]/AS$$

$$PO_4^{-3}, \text{ percent} \times 1{\cdot}65 = (2\,\text{TSP} \times 1\,\text{DSP})$$

$$\text{Total } PO_4, \text{ percent} = [(ME - PE) \times N \times 9{\cdot}5)]/AS$$

$$(2\,\text{TSP} + 1\,\text{DSP}), \text{ percent} = [(ME - PE) \times N \times 15{\cdot}7]/AS$$

where

PE = millilitres of HCl used to obtain the phenolphthalein end point,

ME = millilitres of HCl used to obtain the mixed indicator end point,

N = normality of the HCl,

A = millilitres of sample titrated, and

S = specific gravity of the sample.

8. TOTAL COPPER IN ACID (IODOMETRIC)

8.1 Principle — The copper in the sample is oxidized with potassium permanganate ($KMnO_4$) and the excess permanganate reduced with hydrazine sulphate ($NH_2NH_2.H_2SO_4$). Any iron present is complexed with ammonium bifluoride (NH_4HF_2). Iodine is liberated by reaction of the copper with potassium iodide (KI) in proportion to the amount of copper present, and the free iodine is titrated with standard sodium thiosulphate ($Na_2S_2O_3$) solution in the presence of a starch indicator.

8.2 Reagents

8.2.1 *Ammonium Bifluoride* — Crystals.

8.2.2 *Hydrazine Sulphate Solution* — 150 g/l.

8.2.3 *Potassium Iodide* — Crystals.

8.2.4 *Potassium Permanganate Solution* — 20 g/l.

8.2.5 *Standard Sodium Thiosulphate Solution* — 0·1 N.

8.2.6 *Starch Indicator Solution*

8.3 Procedure

8.3.1 Pipette an aliquot of the filtered sample into an Erlenmeyer flask containing 25 to 50 ml of water. The aliquot should contain enough copper to give a thiosulphate titration of over 5 ml.

8.3.2 Add $KMnO_4$ solution dropwise until a permanent light pink colour is obtained.

8.3.3 Add hydrazine sulphate solution dropwise until the pink colour disappears. Add 1 to 2 drops in excess.

8.3.4 Add 6 g of ammonium bifluoride (NH_4HF_2) to the flask and dissolve it in the sample.

8.3.5 Add 5 g of potassium iodide (KI), stopper the flask, and swirl to dissolve. Allow to stand for about 5 min. The liberated iodine will turn the solution yellow to brown in colour.

8.3.6 Unstopper the flask and titrate with 0·1 N $Na_2S_2O_3$ solution until most of the reddish-brown colour disappears. Do not titrate to light yellow colour.

8.3.7 Add several drops of starch indicator solution and continue the titration until the purple starch–iodine colour in the solution disappears.

8.3.8 Record the millilitres of $Na_2S_2O_3$ solution used (*A*).

8.4 Calculation

8.4.1 Calculate the total copper in the sample as follows:

$$\text{Copper, percent} = (AN/BS) \times 6{\cdot}4$$

where

A = millilitres of $Na_2S_2O_3$ solution required for the titration,

N = normality of $Na_2S_2O_3$ solution,

B = millilitres of sample titrated, and

S = specific gravity of the sample.

9. COPPER IN HYDROCHLORIC ACID CONTAINING COPPER COMPLEXORS, INORGANIC ACID AND IN MIXTURES OF ORGANIC ACIDS (PHOTOMETRIC)

9.1 Principle — Copper forms a complex with diethyldithiocarbamate that can be extracted from aqueous solution with *o*–dichlorobenzene. The optical density of the yellow-coloured complex is proportional to the amount of copper present in the extract.

9.2 Interference

9.2.1 Ferrous iron interference is eliminated by persulphate oxidation and citrate complexation.

9.2.2 Nickel interferes in this method. It reacts the same as copper.

9.3 Apparatus

9.3.1 *Photometer* — Filter photometer suitable for measurements at a wavelength of 480 to 490 nm (acceptable transmittancy measurements can be made in the range from 450 to 510 nm). Filter photometers and photometric practices prescribed in this method shall conform to standard recommended practices.

9.4 Reagents

9.4.1 *Ammonium Hydroxide* — 1 : 1.

9.4.2 *Ammonium Persulphate* — Crystals.

9.4.3 *Citric Acid* — 250 g/l. Dissolve 125 g of acid in water and dilute to 500 ml.

9.4.4 *Copper, Stock Solution* (1 ml = 0·5 mg Cu)—Dissolve 0·5 g of pure copper wire or sheet in a mixture of 5 ml concentrated nitric acid (sp gr 1·42) and 20 ml of water. Boil to remove nitrous oxide. Cool and dilute to 1 litre with water.

9.4.5 *Copper, Standard Solution* (1 ml = 0·025 mg Cu) — Pipette 5 ml of copper stock solution into a 100 ml volumetric flask and dilute to 100 ml with water.

9.4.6 *DEDTC Solution* (2 g/l) — Dissolve 1 g of sodium diethyldithiocarbamate and 2 g of disodium ethylenediamine tetra acetate in water and dilute solution to 500 ml.

9.4.7 *O-chlorobenzene* ($C_6H_4Cl_2$) — This solvent must be stored in glass. Storage in polyolenin bottles will cause interference in the method.

9.4.8 *Hydrochloric Acid* — 1 : 1.

9.5 Calibration

9.5.1 Follow the procedure of **9.6.2** to **9.6.5** using appropriate volumes of the standard copper solution (0·025 mg Cu/ml) for the photometer being used. If 1, 2, 3, 4 and 5 ml of standard copper solutions are used, the copper concentrations in the 25 ml portions of *o*-dichlorobenzene will be 1, 2, 3, 4 and 5 mg of Cu/l, respectively.

9.5.2 Plot milligrams of Cu per litre on the abscissa and percent transmittance on the ordinate of semilog graph paper.

9.6 Procedure

9.6.1 Pipette 10 ml (V_1) of the filtered sample into a 100 ml volumetric flask. Add 2·5 g of ammonium persulphate and acidify with 20 ml of hydrochloric acid (1 : 1). Heat gently until all effervescence ceases. Then heat to boiling and boil for 2 min, cool, and dilute to 100 ml (V_2) with water.

9.6.2 Pipette an aliquot (V_3) into a 125-ml separatory funnel. The aliquot size will depend on the photometer used. From 1 to 5 ml should cover the copper concentration ranges from 0·01 to 0·1 percent.

9.6.3 Add 10 ml each of citric acid solution, ammonium hydroxide (1 : 1) and DEDTC solution, and mix thoroughly. Let it stand for 2 min.

9.6.4 Add exactly 25 ml (V_4) of *o*-dichlorobenzene to the separatory funnel and shake for 2 min. Allow the layers to separate. Filter the

bottom layer through a 19 mm tuft of surgical cotton in a funnel into a photometer cell.

9.6.5 Prepare a reagent blank by following **9.6.2** to **9.6.4** using water for the aliquot (V_3).

9.6.6 Adjust the photometer to 100 percent transmittance with the reagent blank. Measure the transmittance (T, percent) of the sample, using the same or a matched cell, and record it.

9.7 Calculation

9.7.1 Calculate the total copper in the sample as follows:

$$\text{Copper, percent} = [\text{mg Cu/litre from the curve} \times V_2 \times V_4]/(10\,000 \times S \times V_1 \times V_3)$$

where

V_1 = millilitres of original sample,

V_2 = millilitres of sample after dilution,

V_3 = millilitres of diluted sample used in the extraction,

V_4 = millilitres of *o*-dichlorobenzene used to extract V_3, and

S = specific gravity of the sample.

10. COPPER IN AMMONIACAL BROMATE AND PERSULPHATE (PHOTOMETRIC)

10.1 Principle — The intensity of the blue tetra-amino copper (II) complex is measured and is proportional to the copper concentration in the solvent.

10.2 Apparatus

10.2.1 *Photometer* — suitable for measurement at wavelength 700 nm.

10.3 Reagents

10.3.1 *Ammonium Hydroxide* — 1 : 1.

10.3.2 *Ammonium Persulphate* — Crystals.

10.3.3 *Copper Solution Standard* (1 ml = 0·5 mg Cu) — Dissolve 0·500 g of pure copper wire or sheet in a mixture of 5 ml concentrated nitric acid (sp gr 1·42) and 20 ml of water. Boil to remove nitrous oxide. Cool and dilute to 1 litre with water.

10.4 Procedure

10.4.1 *Calibration* — Pipette aliquots of the standard copper solution into 25 ml volumetric flasks and proceed to **10.4.4**. The use of 5, 10, 15 and 20 ml aliquots of the standard will give solutions containing 0·01, 0·02 0·03 and 0·04 percent copper, respectively.

10.4.2 If filtered samples are still turbid, filter again through a membrane filter (0·45 μm).

10.4.3 Add a measured volume (V_1) of filtered sample to a 25 ml volumetric flask. This volume must have a copper content within the calibration curve range.

10.4.4 Add 5 ml of ammonia (1 : 1) and about 0·1 g of ammonium persulphate to the 25 ml flask and dilute to volume with water. Transfer to a photometer cell.

10.4.5 Adjusted photometer to 100 percent transmittance with a water blank.

10.4.6 Determine the transmittance (T percent) of the sample and record.

10.5 Calculation

10.5.1 Calculate the percent copper in the sample as follows:

$$\text{Copper, percent} = [\text{Copper, (from curve)} \times 25]\, V_1 S$$

where

V_1 = millilitres of sample used, and

S = specific gravity of the sample.

11. COPPER IN AMMONIACAL BROMATE AND PERSULPHATE (VOLUMETRIC)

11.1 Principle — The oxidant (bromate or persulphate) in the sample is reduced with sodium sulphite (Na_2SO_3). After acidifying with hydrochloric acid (HCl), the copper in the sample is oxidized with potassium permanganate ($KMnO_4$) and the excess permanganate is reduced with hydrazine sulphate ($NH_2NH_2.H_2SO_4$). Iodine is liberated by the reaction of cupric ion with potassium iodide (KI) in proportion to the amount of copper present. The free iodine is titrated with standard sodium thiosulphate ($Na_2S_2O_3$) solution in the presence of a starch indicator.

11.2 Reagents

11.2.1 *Hydrazine Sulphate Solution*

11.2.2 *Hydrochloric acid* — 1 : 1.

11.2.3 *Potassium Iodide* — Crystals.

11.2.4 *Potassium Permanganate Solution* — 10 g/l.

11.2.5 *Sodium Sulphide Solution* — Saturated. A saturated solution will contain about 200 g/l.

11.2.6 *Standard Sodium Thiosulphate Solution* — 0·1 N.

11.2.7 *Starch Indicator Solutian*

11.3 Procedure

11.3.1 Pipette an aliquot of the sample into a 250 ml Erlenmeyer flask containing 30 to 50 ml of water. This aliquot should contain enough

copper to react with 5 to 15 ml of 0·1 N sodium thiosulphate solution.

11.3.2 Add at least 4 ml of saturated Na_2SO_3 solution to the sample for each 1 percent of bromate or persulphate in the original copper solvent. Allow to react for 2 to 3 min.

11.3.3 Add 5 ml of HCl (1 : 1). The first portions of the acid should be added dropwise with vigorous shaking until the colour disappears. Add the remaining acid rapidly and allow the sample to react for 2 to 3 min. Make certain that all sulphur dioxide (SO_2) has been removed.

11.3.4 Add $KMnO_4$ solution dropwise with vigorous swirling until a permanent light pink colour is obtained.

11.3.5 Add saturated hydrazine sulphate solution dropwise until the solution is clear and then add 1 to 2 drops in excess.

11.3.6 Add 1 to 2 g of KI to the flask, stopper, swirl to mix and let stand for 5 min.

11.3.7 Titrate the solution with the 0·1 N $Na_2S_2O_3$ solution until the brown colour starts to disappear.

11.3.8 Add 10 drops of starch indicator solution and continue the titration until the blue black colour disappears for approximately 30 s.

11.3.9 Read and record the millilitres of $Na_2S_2O_3$ solution used (*A*).

11.4 Calculation

11.4.1 Calculate the percent copper in the solvent as follows:

$$\text{Copper, percent} = (AN/BS) \times 6{\cdot}4$$

where

A = millilitres of $Na_2S_2O_3$ solution used in the titration,

N = normality of the $Na_2S_2O_3$ solution,

B = millilitres of sample titrated, and

S = specific gravity of the sample.

12. TOTAL IRON IN ACID (IODOMETRIC)

12.1 Principle — The iron in the sample is oxidized to ferric state using potassium permanganate ($KMnO_4$). The excess $KMnO_4$ is reduced with hydrazine sulphate ($NH_2NH_2.H_2SO_4$). Potassium iodide (KI) is added and the iodine, liberated by reaction of KI with ferric ions, is titrated with standard sodium thiosulphate ($Na_2S_2O_3$) solution.

12.2 Reagents

12.2.1 *Hydrazine Sulphate Solution* — 150 g/l. Dissolve 15 g of grannular hydrazine sulphate in 100 ml of water.

12.2.2 *Hydrochloric Acid* — 1 : 1.

12.2.3 *Potassium Iodide* — Crystals.

12.2.4 *Potassium Permanganate Solution* — 20 g/l.

12.2.5 *Standard Sodium Thiosulphate Solutiom* — 0·1 N.

12.2.6 *Starch Indicator Solution*

12.3 Procedure

12.3.1 Pipette an aliquot of the filtered sample into an Erlenmeyer flask containing 25 to 50 ml of water. If iron is being determined in an organic acid solvent, add 5 ml of HCl to the sample. The aliquot should contain sufficient iron to give a titration of 5 to 15 ml of $Na_2S_2O_3$ solution.

12.3.2 Add $KMnO_4$ solution dropwise until a permanent pink colour is obtained.

12.3.3 Add hydrazine sulphate solution dropwise until the pink colour disappears, add 1 to 2 drops in excess.

12.3.4 Add approximately 5 g of KI, stopper the flask and swirl to dissolve. Let stand for about 5 min. The liberated iodine will turn the solution yellow to brown in colour.

12.3.5 Unstopper the flask and titrate with 0·1 N $Na_2S_2O_3$ solution until most of the brown colour disappears.

12.3.6 Add several drops of starch indicator solution and continue the titration until the solution is colourless.

12.3.7 Record the millilitres of $Na_2S_2O_3$ solution used (*A*).

12.4 Calculation

12.4.1 Calculate the total iron in the sample as follows (*see* **12.4.2**) :

$$\text{Iron, percent} = (AN/BS) \times 5{\cdot}5$$

where

A = millilitres of $Na_2S_2O_3$ solution required for the titration,

N = normality of the $Na_2S_2O_3$ solution,

B = millilitres of sample titrated, and

S = specific gravity of the sample.

12.4.2 If the sample contains copper:

$$\text{Iron, percent} = [(A - C)N \times 5{\cdot}5]/BS.$$

where

C = millilitres of $Na_2S_2O_3$ solution used to titrate copper in **11.3.9**. The same volume must be used for both iron and copper titrations.

13. IRON BY THE THIOGLYCOLLATE METHOD (PHOTOMETRIC)

13.1 Principle — Iron and thioglycollic acid in solutions buffered from *p*H 9·0 to 10·0 form a

red-purple complex, the colour intensity of which is proportional to the concentration of iron in the sample.

13.2 Interferences — The interferences in this method are the organic components present in some solvents that form strong complexes with the metals in the solution. A procedure to eliminate these interferences is provided.

13.3 Apparatus

13.3.1 *Photometer* — suitable to operate at 540 nm.

13.4 Reagents

13.4.1 *Ammonium Persulphate*

13.4.2 *Buffer Solutions* — Dissolve 33·8 g of ammonium chloride in 100 ml of water and add 285 ml of concentrated ammonium hydroxide. Dilute to 500 ml with water.

13.4.3 *Citric Acid Solution* — 100 g/l.

13.4.4 *Hydrochloric Acid* — 1 : 1.

13.4.5 *Iron Solution Stock* (1 ml = 1 mg of iron) — Dissolve 0·702 2 g ferrous ammonium sulphate [$Fe(NH_4)_2(SO_4)_2.6H_2O$] in water containing 1 ml of concentrated hydrochloric acid and dilute to 100 ml.

13.4.6 *Nitric Acid* — 1 : 1.

13.4.7 *Thioglycollate Solution* — Saturate 500 ml of water with 70 g of anhydrous sodium sulphite. Add 30 ml of thioglycollic acid and 50 ml of concentrated ammonium hydroxide.

13.5 Procedure

13.5.1 *Calibration*

13.5.1.1 Pipette appropriate aliquots of standard iron solution (1 ml = 0·1 mg Fe) into 100 ml volumetric flasks. The use of 1, 2, 3, 4 and 5 ml of the solution will give standards containing 1, 2, 3, 4 and 5 mg Fe/l. To process, follow the procedure starting with **13.5.5.**

13.5.1.2 Plot milligrams of Fe per litre on the abscissa and the transmittance (T, percent) on the ordinate of a semilog graph.

13.5.2 If the solvent contains no copper complexes, gluconates, or various ethylenediamine tetra acetate type organics, pippette 5 ml (V_1) of filtered sample into a 100 ml volumetric flask. Add 10 ml of citric acid solution, dilute to 100 ml (V_2) and proceed to **13.5.4.**

13.5.3 If the solvent contains organic agents, pipette 5 ml (V_1) of the filtered sample into a 100 ml volumetric flask. Slowly and cautiously, add dropwise 10 ml of HNO_3. Let stand until all effervescence ceases. Heat gently and gradually bring the solution to a boil, volatilizing all of the nitrous oxide, and continue heating to near dryness; allow the flask to cool. Add 1 g of HCl. The rate of addition will be determined by the vigour of the persulphate-organic reaction in the flask. Heat gently after the addition of HCl until the effervescence subsides, then boil for 2 min. Cool and add 10 ml of citric acid solution. Dilute to 100 ml (V_2).

13.5.4 Pipette a 1 ml (V_3) aliquot into a 100 ml flask.

13.5.5 Add 10 ml of buffer solution and 2 ml of thioglycollate solution and dilute to 100 ml (V_4).

13.5.6 Adjust the photometer to 100 percent transmittance with a water blank.

13.5.7 Measure the transmittance (T, percent) of the sample and record.

13.6 Calculation

13.6.1 Calculate the iron content of the sample as follows:

$$\text{Iron, percent} = [\text{mg Fe/l from the curve} \times V_2 \times V_4]/(10\,000 \times S \times V_1 \times V_3)$$

where

V_1 = millilitres of original sample,

V_2 = millilitres of sample after initial dilution,

V_3 = millilitres of diluted sample used to test,

V_4 = millilitres of sample after final dilution, and

S = specific gravity of the sample.

14. CALCIUM IN SOLVENTS (VOLUMETRIC)

14.1 Principle — The acidic solvent is treated with activated charcoal to remove organic surfactants and acid inhibitors. An aliquot of the treated solvent is acidified and oxidized with ammonium persulphate $(NH_4)_2S_2O_8$ or bromine water. Magnesium chloride ($MgCl_2$) is added to improve titration end point detection. The aliquot is reacted with an excess of EDTA. Triethanolmine and potassium hydroxide (KOH) are added to the solution to raise the H from 12·5 to 13 and complex the iron in the aliquot. Sodium sulphide-borate buffer is added to complex divalent heavy metals (Cu, Zn). The colour of the solution containing calcium indicator is blue when excess EDTA is present. The excess EDTA is back titrated with calcium standard solution. The calculation of calcium content is based on the quantity of EDTA required to react with calcium in the aliquot.

14.2 Interference

14.2.1 The major interferences in this method of analysis are di- and trivalent metals and phos-

phates. Triethanolamine is added to complex ferric iron and aluminium. The quantity of iron in the sample being titrated should not exceed 75 mg.

14.2.2 Copper and zinc are removed by the addition of sodium sulphide-borate buffer solution. The quantity of copper in the sample should not exceed 25 mg.

14.2.3 The phosphate ion is prevented from interfering by keeping the amount of uncomplexed calcium at a very low level. The phosphate ion is the reason for the back titration method used in the procedure.

14.2.4 The absence of magnesium may be considered an interference in that the indicator will not show consistent colour changes in the absence of magnesium ions.

14.3 Reagants

14.3.1 *Ammonium Persulphate* — crystals.

14.3.2 *Calcium Indicator* (Solochrome Dark Blue or Eriochrome Blue Black R (sodium 1 - (2 - hydroxy-1-naphthylazo) - 2-naphthol - 4-sulphonate) - Grind 0·1 g of the indicator reagent with 20 g of sodium chloride (NaCl) to a fine powder.

14.3.3 *Standard Calcium Solution* (1 ml = 1·00 mg Ca) — Dissolve 2·75 g of $CaCO_3$ in a minimum of hydrochloric acid (HCl) (1 : 1) and boil gently to remove carbon dioxide $(CO)_2$. Add a few drops of methyl red indicator solution. Add diluted KOH solution (300 g KOH/l diluted 1 : 19) until just alkaline to methyl red. Add HCl (1 : 9) until just acid to methyl red. Dilute to 1 litre with water and standardize, store in a glass or plastic bottle.

14.3.4 *Activated Charcoal* (*Calcium and Magnesium Free*) — Slurry activated charcoal in HCl (1 : 1). Heat to near boiling and filter while hot. Wash several times with hot water. Test the filtrate after each washing with *p*H paper until washings show no acid. Dry the treated charcoal thoroughly at 120°C. Grind to a fine powder and store in a plastic or glass bottle.

14.3.5 *Standard EDTA Solution* (1 ml = 1 mg Ca) — Dissolve extractly 9·316 g of disodium ethylenediamine tetra acetate dehydrate powder in 800 ml of water and dilute to 1 litre.

14.3.6 *Hydrochloric Acid* — 1 : 1.

14.3.7 *Magnesium Chloride* (40 g/l) — Dissolve 4 g of magnesium chloride ($MgCl_2.6H_2O$) in water and dilute the solution to 100 ml.

14.3.8 *Methyl Red Indicator*

14.3.9 *Sodium Sulphide-Borate Buffer Solution* — Prepare as follows:

Dissolve 40 g of sodium tetraborate ($Na_2B_4O_7.10H_2O$) in 800 ml of water. Dissolve 10 g each of sodium hydroxide, sodium sulphide and potassium sodium tartrate (K Na $C_4H_4O_6.4H_2O$) in 100 ml of water. When cool, mix the two solutions and add 1 g of magnesium ethylene diamine tetra acetate, having a ratio of 1 Mg: 1ETDA. Complex any excess magnesium with standard sodium ethylene diamine tetra acetate solution (1 ml = 1·0 mg $CaCO_3$), if necessary. Make up to 1 litre with water. Keep the solution bottle stoppered when not in use. The reagent will be effective for at least one month.

14.3.10 *Potassium Hydroxide Solution* — 300 g/l.

14.3.11 *Triethanolamine Solution* — 250 g/l.

14.4 Procedure

14.4.1 *Standardization*

14.4.1.1 This procedure is used to determine the calcium content of the solution prepared in **14.3.3** and the dilution required for a calcium standard having 1 ml = 1·00 mg Ca.

14.4.1.2 From a burette, add 10 ml of calcium solution to a 400-ml beaker and add 100 ml of water. Do not refill the burette.

14.4.1.3 From a burette, add 15 ml of EDTA titrant.

14.4.1.4 Add 1 ml of magnesium solution, 15 ml each of triethanolamine and KOH solution, 1 to 1·5 ml of sodium sulphide-borate buffer solution and mix. Check the *p*H electrometrically. The *p*H must be between 12·5 and 13. If the *p*H is less than 12·5, adjust upward with KOH solution. If greater than 13, discard and repeat **14.4.1.2** using less KOH solution and adjusting the *p*H upward, if necessary.

14.4.1.5 Add 0·05 g of calcium indicator. Titrate slowly with calcium solution to the end point. Continuous stirring is required for this titration. The colour change is from blue through purple near end point to pure red at the end point. Record the total volume (A) of calcium solution used.

14.4.1.6 Fifteen millilitres of EDTA solution should be equivalent to 15 ml of calcium standard. To prepare 500 ml of standard with 1 ml = 1 000 mg Ca dilute ($300 \times A/15$) ml of calcium solution to 500 ml with water where A = 1 millilitre of calcium solution used in the titration.

14.4.2 Add approximately 3 g of calcium and magnesium-free activated charcoal to approximately 100 ml of sample. Agitate with a magnetic stirrer for at least 10 min. Filter through a 0·45 μm membrane filter.

14.4.3 Pipette 50 ml (V_1) of the filtrate into a 250 ml volumetric flask. Add 20 ml of HCl

(1 : 1) and either 2 g of ammonium persulphate or approximately 30 ml of saturated bromine water. Boil for at least 10 min or until all bromine has been expelled if bromine water was used as the oxidant. Cool and dilute to 250 ml (V_2) with water.

14.4.4 Pipette an aliquot (V_3, Ca) of dilute solution prepared in **14.4.3** into a 400 ml beaker (25 ml aliquot has generally proven adequate on field samples). Add approximately 100 ml of water. The aliquot should contain less than 75 mg of iron and calcium ions equivalent to 10 to 20 mg of EDTA standard.

14.4.5 All additions from this point in the procedure should be made with continuous stirring. A magnetic stirring device is recommended. From a burette, add a volume of EDTA titrant, for example, 20 ml, sufficient to complex calcium in the aliquot plus 5 to 8 ml excess. Do not refill the burette. Record as ml EDTA (1).

14.4.6 Add 1 ml of magnesium solution, 15 ml each of triethanolamine and KOH solution, and 1 to 1·5 ml of sodium sulphide-borate buffer solution. Check the *p*H with a *p*H meter. The *p*H must be between 12·5 and 13, adjust upward with KOH solution. If greater than 13, discard and repeat **14.4.4** and **14 4.5**, using less KOH solution and adjusting the *p*H upward as required.

14.4.7 Add 0·05 g of calcium indicator and titrate slowly with calcium standard to near the end point (blue through purple near the end point to pure red at the end point). The solution should be clear blue prior to titration with calcium titrant. If the colour is not clear blue, add EDTA titrant until the solution turns blue. Then add 5 ml excess. As the end point is approached, add calcium standard in 2-drop increments, waiting between each addition to observe the colour change. Note the burette reading after each addition. The correct end point reading is that reading prior to the last two drops addition that produces no further colour change. Record this reading as ml Ca (1) Subtract this value from ml EDTA (1) in **14.4.5**. Record the difference as Ca (1). Do not refill the burette.

NOTE — Near the end point, the magnesium hydroxide [$Mg(OH)_2$] floc will suddenly adsorb a large portion of the indicator dye and thereby become visible. If the floc is allowed to settle, it will be coloured a definite blue if unreacted EDTA is present, and red in the presence of very slight excess of calcium.

14.4.8 Continue the titration with EDTA blue. Add about 0·5 ml additional and record this new reading as ml EDTA (2).

14.4.9 Allow about 10 s of time to elapse and resume titration with calcium standard to a red point as in **14.4.7** to obtain a [1 ml Ca (2)] value. Substract [ml Ca (2)] from [1 ml EDTA (2)] to obtain a Ca (2) value.

14.4.10 Repeat **14.4.8** and **14.4.9** once or twice more if a more reliable average is desired. Average the separate Ca (n) values and record as Ca (av). Reject any Ca (n) value that differ from the average by more than 0·20 ml. Use the remaining values to recalculate a new average.

14.5 Calculation

14.5.1 Calculate calcium content of the sample as follows:

$$\text{Calcium, percent} = (V_2 \times 0{\cdot}1 \times \text{Ca (av)}) / [\, V_1 \times (V_3, \text{Ca}) \times S \,]$$

where

V_1 = millilitres of original aliquot diluted to V_2 in **14.4.3**,

V_2 = millilitres to which V_1 was diluted,

V_3, Ca = millilitres of V_2 used in titration,

Ca (av) = average millilitres of EDTA that reacted with calcium in the sample (ml EDTA standard – ml calcium standard) obtained in **14.4.5** through **14.4.10** inclusive, and

S = specific gravity of the sample.

14.5.2 The above equation is valid only when the EDTA titrant and calcium standard titres are equivalent and equal to 1·00 mg Ca/ml. If the EDTA titrant and calcium standard do not contain the equivalent of 1·00 mg Ca/ml, the following correction should be made in calculating ml Ca in **14.4.5** through **14.4.10** inclusive.

$$[\text{ml EDTA (1)}] = (\text{ml EDTA added}) \times (\text{mg Ca/ml EDTA})$$

$$[\text{ml Ca (1)}] = (\text{ml calcium added}) \times (\text{mg Ca/ml calcium standard})$$

15. MAGNESIUM IN ACID SOLVENTS (VOLUMETRIC)

15.1 Principle—The acidic solvent is treated with activated charcoal to remove the surfactant and acid inhibitors. An aliquot of the treated solvent is acidified and oxidized with ammonium persulphate $(NH_4)_2S_2O_8$ or bromine. Tartaric acid is added to complex iron and the *p*H is adjusted with ammonium hydroxide (NH_4OH). Excess of EDTA standard solution is added. The solution is buffered to *p*H 10 and triethanolamine and sodium sulphide-borate buffer solutions are added. The *p*H is again adjusted to 10.0 to 10.2 with potassium hydroxide (KOH). Eriochrome Black T indicator is added and the excess EDTA is back titrated with a standard calcium solution. The calculation of magnesium content is based on difference in quantities of EDTA required to react with (1) calcium plus magnesium and (2) calcium in the sample.

15.2 Interference — The interferences for the combined calcium and magnesium determination are the same as those defined in the calcium procedure (*see* **14.2.1** to **14.2.3**).

15.3 Reagents

15.3.1 *Ammonium Hydroxide* — sp gr 0·90.

15.3.2 *Ammonium Persulphate* — crystals.

15.3.3 *Buffer Solution* — *see* **14.3.9**.

15.3.4 *Standard Calcium Solution* (1 ml = 1·00 mg Ca)

15.3.5 *Standard EDTA Solution* (1 mg = 1 mg of calcium)

15.3.6 *Erichrome Black T indicator*

15.3.7 *Hydrochloric Acid* (1 + 1)

15.3.8 *Methyl Red Indicator*

15.3.9 *Potassium Hydroxide Solution* (300 g/l.)

15.3.10 *Tartaric Acid* (*crystal*)

15.4 *Procedure*

15.4.1 Standardize as given in **14.4.1**.

15.4.2 Pipette an aliquot (V_3, Ca + Mg) of the sample treated as in **14.4.3** into a 400 ml breaker (25 ml aliquot has generally proven adequate on field samples). Add approximately 100 ml of water, 3 to 4 drops of methyl red indicator solution, and 1 g of tartaric acid. The aliquot should contain less than 75 mg of iron and a quantity of calcium plus magnesium equivalent to 10 to 25 ml of EDTA standard.

15.4.3 All additions from this point in the procedure should be made with continuous stirring. A magnetic stirring device is recommended. Add from a burette, a volume of EDTA titrant sufficient to complex the calcium and magnesium and give an excess of 5 to 8 ml. Do not refill the burette.

15.4.4 And 15 ml of triethanolamine solution. Add NH_4OH until alkaline to methyl red and 2 to 3 ml in excess. Then add 1 to 1·5 ml of sulphide-borate buffer solution.

15.4.5 With a *p*H matter, adjust the *p*H to 10·0 to 10·2 with KOH solution. About 2 ml of 300 g/l KOH solution should suffice.

15.4.6 Add about 0·05 g of Eriochrome Black T indicator powder. This amount of indicator will give optimum depth of colour in which slight changes in at colour and near the end point are most discernible. Too large amount of indicator should be avoided. At this point in the determination, the colour sholud be clear blue or blue green. If insufficient EDTA is present to completely complex the calcium and magnesium present, the colour will be red or blue tinged with red. If this should occur, add a measured additional amount of EDTA titrant to give an excess.

15.4.7 From a second burette, titrate slowly with standard calcium to a definite red colour. Add 4 to 5 drops in excess and record the calcium titrant volume [ml Ca (1)]. Do not refill the burette.

15.4.8 Resume the titration with EDTA titrant. Add titrant slowly near the end point. When close to the end point, add the EDTA by 2-drop increments, noting the reading on burette after each addition. The correct end point is that reading noted prior to the last 2-drop addition that produces no colour change. Record as [ml EDTA (1)]. Subtract [ml Ca (1)] [ml Ca (1)] to obtain (Ca + Mg) (1).

15.4.9 Without refilling the burette, add about 1 ml of additional EDTA titrant. Change to the second burette and add slowly sufficient calcium titrant to obtain a red end point and then a few drops in excess. Record this second reading as [ml Ca (2)].

15.4.10 Without refilling the burrette, continue the titration with EDTA titrant to a second end point recorded as [ml EDTA (2)]. Subtract [ml Ca (2)] from this value to obtain (Ca + Mg) (2).

15.4.11 Repeat **15.4.9** and **15.4.10** once or twice more if a more reliable average (Ca + Mg) values and record as (Ca + Mg) (av). Reject any (Ca + Mg) value that differs from the average by more than 0·20 ml. Use the remaining values to calculate a new average.

15.5 Calculation

15.5.1 Calculate the magnesium content of the sample as follows:

$$\text{Magnesium, percent} = \frac{V_2 \times [(\text{Ca} + \text{Mg})\,(\text{av}) - \text{Ca}\,(\text{av})] \times 0{\cdot}06}{V_1 \times V_3\,(\text{Ca} + \text{Mg}) \times S}$$

where

V_1 = millilitres of sample diluted to V_2 in **14.4.3**;

V_2 = millilitres to which V_1 was diluted in **14.4.3**;

V_3 = (Ca + Mg) millilitres of diluted sample titrated in the procedure, (Ca + Mg) (av) = millilitres of EDTA standard solution that reacted with the Ca + Mg in **15.4.9**, **15.4.10** and **15.4.11**;

Ca(av) = millilitres of EDTA solution standard that reacted with calcium in the aliquot (V_3) as determine in **14.4.8** (V_3, Ca in **14.4.4** must be the same volume as V_3, Ca + Mg in **15.4.2**); and

S = specific gravity of the sample.

16. SILICA IN ACID AND ALKALINE SOLVENTS (GRAVIMETRIC)

16.1 Principle — Silicon compounds in the solvent are concentrated and precipitated as partially dehydrated SiO_2 by evaporation with hydrochloric acid (HCl). Dehydration is completed by ignition, and silica is volatilized as silicon tetrafluoride (SiF_4).

16.2 Interferences — The anions and cations generally found in cleaning solvents do not interfere.

16.3 Reagents — It is recommended that all reagents given below be stored in polyethylene bottles.

16.3.1 *Methyl Orange Indicator* — Dissolve 0·1 g of methyl orange in distilled water and dilute to 1 litre.

16.3.2 *Concentrated Hydrochloric Acid* — *See* IS : 265-1987*.

16.3.3 *Dilute Hydrochloric Acid* — Dilute 2 volumes of concentrated hydrochloric acid with 98 volumes of distilled water.

16.3.4 *Concentrated Sulphuric Acid* — *See* IS : 266-1977†.

16.3.5 *Hydrofluoric Acid* — 48 to 51 percent (m/m).

16.4 Procedure

16.4.1 Test the sample with methyl orange indicator. If the sample is alkaline to methyl orange, add to a volume of the sample containing not less than 5 mg of silica (as SiO_2) sufficient concentrated hydrochloric acid to neutralize it and provide a 5-ml excess of the acid. If the sample is originally acid to methyl orange, add only 5 ml of concentrated hydrochloric acid without any neutralization. Evaporate the acidified sample to approximately 100 ml in a 400-ml, scratch-free, low-form, chemically resistant glass beaker (*see* Note) on a water-bath or hot-plate, under a fume hood. Add 5 ml of hydrochloric acid and continue to evaporate the sample to dryness in a water-bath with periodic additions of three more 5 ml increments of hydrochloric acid. Dry the evaporated residue in an oven at 110°C for one hour.

NOTE — If the silica content is so low that a very large quantity of the sample has to be evaporated, do not increase the size of the beaker but periodically replenish the evaporating liquid with increments from the acidified sample reservoir.

16.4.2 Add 5 ml of hydrochloric acid and then 50 ml of water to the dried residue in the beaker, warm the beaker and its contents and stir the mixture with a rubber policeman to dissolve or suspend all of the residue. Filter the warm solution through an ashless medium texture paper. Wash the residue on the paper fifteen times with 1 : 49 hydrochloric acid and then with several small increments of water. Cover the funnel containing the paper and its residues with a clean watchglass and reserve it for later ignition.

16.4.2.1 Return the filtrate from **16.4.2** to the original evaporating beaker, and evaporate to dryness on a water-bath with periodic additions of two 5 ml increments of hydrochloric acid. Dry and repeat the filtration and washings described in **16.4.2** using a second funnel and filter paper. Place both the filter papers with their dehydrated residue in a weighed platinum crucible, dry and char the paper without flaming it and then ignite the charred residue for 30 minutes at 1 000 to 1 200°C. Cool in a desiccator and weigh. Repeat ignition until a constant mass is obtained (W_1).

16.4.3 To the weighed residue, add several drops of concentrated sulphuric acid and 5 ml of hydrofluoric acid and evaporate to dryness on a low-temperature hot-plate or water-bath under a fume hood. Re-ignite the residue at 1 000 to 1 200°C to constant mass (W_2).

16.4.4 Carry out a blank by making an identical determination on the quantity of distilled water required for washing and diluting in **16.4.2** and **16.4.2.1**.

16.5 Calculation

$$\text{Silica (as } SiO_2\text{), mg/l} = \frac{(W_1 - W_2) - (W_3 - W_4)}{V}$$

where

W_1 = mass in mg of the residue obtained in **16.4.2**,

W_2 = mass in mg of the residue obtained in **16.4.3**,

W_3 = mass in mg of the residue before treatment with hydrofluoric acid in **16.4.4**,

W_4 = mass in mg of the residue after treatment with hydrofluoric acid in **16.4.4**, and

V = volume in litres of the sample taken for the test.

17. SILICA IN ALKALINE PHOSPHATE SOLUTIONS (PHOTOMETRIC)

17.1 Principle — The phosphate in the solvent is precipitated with zinc after acidification of the sample. The surfactants in the solvent are removed with activated charcoal. Ammonium molybdate is added and the blue silicomolybdate

*Specification for hydrochloric acid (*third revision*).

†Specification for sulphuric acid (*second revision*).

colour is developed with amino naphthol sulphonic acid and is proportional to the soluble reactive SiO_2 concentration in the solvent.

17.3 Interferences

17.2.1 The primary interference of this method is the high ratio of phosphate ion concentration to the low SiO_2 concentration. These solvents may contain as high as 1 percent alkaline phosphates while the maximum SiO_2 is somewhat less than 100 mg of SiO_2/l (0·1 percent SiO_2) The interference is largely overcome by precipitation of the phosphates.

17.2.2 The various surfactants used in these solvents change the silicomolybdate colour reaction.

17.2.3 Some of the SiO_2 is adsorbed on zinc phosphate and activated charcoal in the preparatory steps. This can be minimized by thoroughly washing the charcoal and precipitate.

17.2.4 The volumetric glassware and pipettes should be thoroughly acid leached prior to use in this SiO_2 procedure. The chemicals used must contain very low concentrations of silica. This interference may be detected by running a blank.

17.3 Apparatus

17.3.1 *Filter Photometer* — Filter photometer suitable for measurement at a wavelength of 815 nm. Acceptable measurements can be made in the range 640 to 700 nm, however, with some sacrifice in precision.

17.4 Reagents

17.4.1 *Amino Naphthol-Sulphuric Acid Solution*

17.4.2 *Ammonium Molybdate Solution* — 100 g/l.

17.4.3 *Charcoal, Activated, Silica Free* — Weigh 50 g of activated charcoal into a one-litre polyethylene bottle. Add 25 g ammonium bifluoride (NH_4HF_2) crystals and fill two-thirds full with hydrochloric acid [HCl, 1 part concentrated HCl (sp gr 1.19) + 3 parts water). Stir with a magnetic stirrer for at least 2 h. Filter through a plastic Buchner funnel with a highly retentive filter paper. Wash with water several times until the filtrate is free of chlorides. Dry the treated charcoal overnight at 160°C. Grind to a fine powder, if necessary.

17.4.4 *Hydrochloric Acid* — 1 ; 1.

17.4.5 *Oxalic Acid* — 100 g/l.

17.4.6 *Phenolphthalein Indicator Solution* — 10 g/l.

17.4.7 *Stock Solution, Silica* — (1 ml = 1 mg of SiO_2) — Dissolve 4·73 g sodium metasilicate nanohydrate ($Na_2SiO_3.9H_2O$) in recently boiled and cooled water and dilute to 1 litre. Store in a plastic bottle.

17.4.8 *Standard Solution of Silica* (1 ml = 0·02 mg SiO_2)—Dilute 20 ml of stock solution to 1 litre with water.

17.4.9 *Zinc Oxide Powder*

17.4.10 *Zinc Sulphate Solution* — 150 g/l.

17.5 Procedure

17.5.1 *Calibration* — Pipette appropriate aliquots of the standard silica solution into 50 ml volumetric flasks. The use of 1, 2, 3, 4 and 5 ml aliquots will give standards containing 0·4, 0·8, 1·2, 1·6 and 2·0 mg/l (ppm) of SiO_2, respectively.

17.5.1.1 Add water to each flask to bring the volume up to about 25 ml. Add 2 ml of HCl and 2 ml of ammonium molybdate solution.

17.5.1.2 Proceed with **17.5.2.4** to **17.5.2.6**.

17.5.1.3 Plot milligrams per litre (ppm) SiO_2 on the abscissa and percent transmittance (T, percent) on the ordinate of a semilog graph paper.

17.5.2 *Procedure* — Pipette 25 ml (V_1) of sample into a 150 ml beaker. Add 2 drops of phenolphthalein indicator solution. Add HCl dropwise until colourless and 5 drops in excess. Add 10 ml of zinc sulphate solution, 0·25 g of activated charcoal, and 0.5 g of zinc oxide powder. Heat to boiling. Filter through a highly retentive paper, while hot. Collect the filtrate in a 100-ml, stoppered, graduated cylinder.

17.5.2.1 Add 20 ml of water to the original beaker, heat to boiling, and wash down the filter with the hot water. Repeat this operation until about 80 ml of filtrate has been collected in the cylinder.

17.5.2.2 Dilute to 100 ml (V_2) with water.

17.5.2.3 Pipette a 25-ml (V_3) aliquot into a 50-ml volumetric flask. Add 2 ml of HCl and 2 ml of ammonium molybdate solution.

17.5.2.4 After 5 min, add 2 ml of oxalic acid solution.

17.5.2.5 After 5 min, add 2 ml of amino naphthol sulphonic acid solution. Dilute to 50 ml (V_4) with water.

17.5.2.6 After 5 min, transfer the solution to a photometer cell and measure the transmittance (T, percent) using a water blank, and record.

17.5.3 *Calculation*

17.5.3.1 Calculate the SiO_2 content of the solvent as follows:

$$SiO_2, \text{ mg/l, ppm} = SiO_2 \text{ (graph)} \times (V_2/V_1) \times (V_4/V_3)$$

where

V_1 = millilitres of sample,

V_2 = millilitres of diluted sample,

V_3 = millilitres of diluted sample used in the test, and

V_4 = millilitres of final aliquot.

18. HYDRAZINE IN PASSIVATING SOLUTIONS (VOLUMETRIC)

18.1 Principle — Hydrazine is reacted with alkaline permanganate to form manganese dioxide (MnO_2). The MnO_2 is reacted with an excess of oxalic acid under acidic conditions. The excess oxalic acid is titrated with permanganate under acidic conditions.

18.2 Interferences — Hydrazine will react with oxygen when hot and exposed to the air. To minimize hydrazine loss, the sample should be taken by filling a bottle to overflowing, sealing it, and cooling to ambient temperature or below as quickly as possible. The analysis should be made as soon as possible after collecting (within 2 h).

18.3 Reagents

18.3.1 *Oxalic Acid Solution* — 20 g/l.

18.3.2 *Standard Potassium Permanganate Solution* — 0·1 N.

18.3.3 *Sodium Hydroxide Solution* — 50 g/l.

18.3.4 *Sulphuric Acid* (1 : 1)

18.4 Procedure — Pipette an aliquot of the filtered sample into a 250-ml Erlenmeyer flask. Adjust the volume with water to approximately 50 ml. Suggested aliquot for 100 mg/l of hydrazine is 25 ml, for 300 mg/l, 10 ml, and for 500 mg/l, 5 ml.

18.4.1 Add 2 ml of NaOH solution, mix, and titrate with 0·1 N $KMnO_4$ solution until a reddish tint is visible over the brown precipitate of MnO_2. Add 2·0 ml of oxalic acid solution and 5 ml of H_2SO_4 to the solution. Heat to 70°C. The solution becomes colourless. If the solution does not clear up, add more oxalic acid and heat. Titrate with more $KMnO_4$ solution until a pink colour persists for 1 min. Record the millilitres of $KMnO_4$ solution used (V_1).

18.4.2 Add the same volume of oxalic acid solution that was added in **18.4.1** to the solution. Continue the titration with $KMnO_4$ solution as before, without refilling the burette. Record this total titration volume (V_2) required for the sample plus the two additions of oxalic acid.

18.5 Calculation

18.5.1 Calculate the hydrazine content of the sample as follows:

$$N_2H_4,\ mg/l = (2V_1 - V_2)\ N \times 8\,000/A$$

where

V_1 = millilitres of $KMnO_4$ solution required for sample + oxalic acid solution added in **18.4.1**,

V_2 = millilitres of $KMnO_4$ solution required for sample + twice the volume of oxalic acid added in **18.4.1** as determined in **18.4.2**,

N = normality of the $KMnO_4$ solution, and

A = millilitres of sample titrated.

19. CHROMIC ACID (VOLUMETRIC)

19.1 Principle — The oxidizing capacity of CrO_3 is reduced with a known excess of reducing agent (ferrous ammonium sulphate). The excess is titrated against a standard oxidant (dichromate) using diphenylamine indicator.

19.2 Reagents

19.2.1 *Diphenylamine Indicator Solution* — 10 g/l.

19.2.2 *Ferrous Ammonium Sulphate Solution* — 0·3 N.

19.2.3 *Potassium Dichromate Solution* — 0·3 N.

19.2.4 *Titrating Acid* — Mix 150 ml each of concentrated sulphuric acid and 70 percent phosphoric acid. Slowly add the mixed acid to 200 ml of water.

19.3 Procedure — Pipette an aliquot (C) of the filtered CrO_3 solution into a 250-ml Erlenmeyer flask. Add approximately 100 ml of water. This aliquot should contain sufficient CrO_3 to react with approximately 5 ml of ferrous ammonium sulphate solution.

19.3.1 Pipette 10 ml (A) of ferrous ammoninm sulphate solution into the flask and add 20 ml of titrating acid.

19.3.2 Add 3 drops of diphenylamine indicator solution. The colour of the solution at this point should be blue-green. If the colour changes to a dark violet upon addition of the indicator solution, insufficient ferrous ammonium sulphate solution was added in **19.3.1**. Add an additional 5 ml of ferrous ammonium sulphate solution. Volume A will now be 15 ml.

19.3.3 Titrate the contents of the flask with 0·3 N potassium dichromate solution to a dark violet end point that remains for 10 s. Record the volume of potassium dichromate solution used (B).

19.4 Calculation

19.4.1 Calculate the percent CrO_3 in the solvent as follows:

$$CrO_3,\ percent = (A - B)\ N \times 3{\cdot}33/CS$$

where

A = millilitres of ferrous ammonium sulphate solution added,

B = millilitres of potassium dichromate solution used for titration,

N = normality of the potassium dichromate solution,

C = millilitres of sample titrated, and

S = specific gravity of the sample.

20. AMMONIUM BIFLUORIDE OR HYDROFLUORIC ACID CONTENT

20.1 Principle — The method exposes a glass surface to the solvent under specified conditions and the resulting dissolution of the glass is proportional to the quantity of fluoride ion from the ammonium bifluoride or hydrofluoric acid present. The weight loss of the glass is used to determine the percent amonium bifluoride or hydrofluoric acid from previous calibration data.

20.2 Reagents and Equipment

20.2.1 *Plastic Containers* — Polyethylene or other plastic bottles or beaker. The containers must be at least 25 mm in diameter and shall hold at least 150 ml. The depth of the solvent must be at least 75 mm. A plastic cover, cap, or watchglass is required.

20.2.2 *Glass Slides* — 75 by 25 mm, microscope slides.

20.2.3 *Acetone*

20.2.4 *Absorbent—Type Paper Tissues*

20.2.5 *Analytical Balance* — Capable of weighing to 0·1 mg.

20.2.6 *Constant Temperature Bath* — 66°C.

20.3 Calibration and Standardization

20.3.1 Prepare the solvent without the fluoride component.

20.3.1.1 For ammonium bifluoride solvents, weigh the amounts of ammonium bifluoride required to obtain the ammonium bifluoride concentration range desired and add to 150 ml of the fluoride-free solvent, that is, 5 percent HCL-10 percent HCL.

20.3.1.2 Follow steps **20.3.3.1** to **20.3.3.3** and **20.3.3.5** in the procedure.

20.3.1.3 Draw a graph of grams weight loss of the glass slide *versus* ammonium bifluoride concentration or prepare a numerical table.

20.3.2 For hydrofluoric acid solvents, pipette or weigh the volume of hydrofluoric acid required into a plastic graduated cylinder and dilute to 150 ml. If other components are in the hydrofluoric acid solvent, prepare a concentrate of the other components such that 100 ml will contain proper concentrations when diluted to 150 ml. Pour 100 ml of this concentrate into a plastic graduated cylinder. Add the quantity of hydrofluoric acid needed for the concentrations desired. Dilute with water to 150 ml. Follow **20.3.1.2** and **20.3.1.3**.

20.3.3 *Procedure*

20.3.3.1 Transfer 150 ml of freshly shaken solvent to a plastic bottle. Cover with a plastic cover, cap, or watchglass. Preheat in a 66°C bath for 30 min.

20.3.3.2 Clean a standard glass microscope slide (25 by 75 mm) with acetone and wipe with absorbent-type paper tissue and weigh on an analytical balance to the nearest 0·1 mg.

20.3.3.3 Immerse the microscope slide completely in the preheated solution for 1 h.

20.3.3.4 Return the heated sample to the original container if desired for further testing.

20.3.3.5 Wash the watchglass in hot water and dry with acetone and paper tissue. Let cool to room temperature. Reweigh the glass slide and calculate the weight loss in grams.

20.4 Calculation — Read the percent ammonium bifluoride direct from Table 2.

NOTE 3 — The determination of hydrofluoric acid content of the solvent can be obtained from the ammonium bifluoride content. Hydrofluoric acid percent-ammonium bifluoride × 0·70.

21. FLUORIDE IN ALKALINE PHOSPHATE CLEANING SOLUTIONS (POTENTIO-METRIC)

21.1 Principle — The fluoride specific ion electrode develops a potential proportional to the logarithm of fluoride ion activity in the sample.

21.2 Interferences — Hydroxide ion interferes with the fluoride specific ion electrode response at *p*H of 9·5 or above. This interference is eliminated by adjusting the *p*H of the sample to neutral values.

21.3 Apparatus

21.3.1 p*H Meter*

21.3.2 *Fluoride Ion Activity Electrode*

21.3.3 *Single Junction Reference Electrode*

21.3.4 *Plot Paper* — 10 percent volume corrected (Gran).

21.4 Reagents

21.4.1 *Acetic Acid Solution* — 6 M.

21.4.2 *Fluoride Solution* — 0·200 M. Dissolve 8·398 g sodium fluoride in water and dilute to 1 litre with water. Store in plastic containers.

TABLE 2 CONVERSION TABLE : GRAMS LOSS (GLASS SLIDE) TO PERCENT AVAILABLE ABF*

(*Clause* 20.4)

GRAM LOSS	PERCENT ABF*	GRAM LOSS	PERCENT ABF*	GRAM LOSS	PERCENT ABF*	GRAM LOSS	PERCENT ABF*
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
0·001	0·03	0·079	0·56	0·240	1·31	0·490	2·46
0·002	0·05	0·083	0·58	0·250	1·36	0·500	2·46
0·003	0·08	0·088	0·60	0·260	1·41	0·510	2·55
0·004	0·09	0·094	0·62	0·270	1·45	0·520	2·60
0·005	0·10	0·100	0·63	0·280	1·50	0·530	2·65
0·006	0·11	0·104	0 68	0·290	1·54	0·540	2·69
0·008	0·12	0·108	0·70	0·300	1·59	0·550	2·74
0·010	0·14	0.112	0·72	0·310	1·63	0·560	2.79
0·015	0·18	0·116	0·74	0·320	1·68	0·570	2·83
0·020	0·22	0·121	0·76	0·330	1·72	0·580	2·88
0·024	0·25	0·125	0·78	0·340	1·77	0·590	2·93
0·029	0·28	0·129	0.80	0·350	1·81	0·600	2·97
0·031	0·30	0·133	0·82	0·360	1·85	0·610	3·02
0·034	0·32	0·138	0·85	0·370	1·91	0·620	3·06
0·038	0·34	0·142	0·86	0·380	1·95	0·630	3·11
0·041	0·36	0·146	0·88	0·390	2·00	0·640	3·15
0·044	0·38	0·150	0·90	0·400	2·04	0·650	3·20
0·048	0·40	0·160	0·95	0 410	2·09	0·660	3·24
0·052	0·42	0·170	0·99	0·420	2·14	0·670	3·29
0·056	0·44	0·180	1·04	0·430	2·18	0·680	3·33
0·059	0·46	0·190	1·09	0·440	2·23	0.6 0	3·38
0·063	0·48	0·200	1·13	0·450	2·28	0·700	3·42
0.067	0·50	0·210	1·18	0·460	2·32	0·710	3·47
0·071	0.52	0·220	1·22	0·470	2·37	0·720	3.51
0·075	0·54	0·230	1·27	0·480	2·41	0.730	3·56

*ABF ammonium bifluoride.

21.4.3 *Fluoride Working Solution* — Dilute 10 ml of fluoride solution (**21.4.2**) to 1 litre with water.

21.4.4 *Mixed Indicator Solution* — Prepare by dissolving 0·05 g of bromocresol green in 50 ml of rectified spirit and 0·075 g of methyl red in 50 ml of rectified spirit. Mix these two solutions well.

21.4.5 *TISAB Solution* (*Tonic Strength Buffer Solution*) — Dissolve 58 g of sodium chloride and 0·30 g of sodium citrate in 500 ml of water. Add 50 ml of glacial acetic acid (sp gr 1·05). While cooling, add 20 percent of sodium hydroxide until the *p*H is between 5·0 and 5·5. Cool to ambient temperature and dilute to 1 litre with water. This solution has a limited shelf life.

21.5 Standardization

21.5.1 Pipette 50-ml aliquot of TISAB solution into a 200-ml plastic beaker. Add 50 ml of water.

21.5.2 Insert electrodes and stir to mix. A magnetic stirrer is preferred. Exercise care to prevent bubbles from being trapped on electrode surfaces.

21.5.3 With the *p*H meter in millivolt mode, allow the readings to stabilize, generally 3 to 5 min, and record the potential.

21.5.4 Add 1 ml of working fluoride solution ($2{\cdot}0 \times 10^{-3}$ M) and record the resultant potential.

21.5.5 Repeat **21.5.4** until 6 additions have been made.

21.5.6 Remove electrodes from solution, rinse well with water, and dry with tissue paper. Store electrodes in water.

21.5.7 Determine the apparent amount of fluoride in the blank by plotting the values obtained in **21.5.3**, **21.5.4** and **21.5.5**. Using Gran's plot paper, plot the millivolts on the ordinate and the millilitres of 2.0×10^{-3} M fluoride solution added on the abscissa. Place the ordinate to allow space for an extrapolated intercept. Draw the best straight line through the last four or five points. Extend this line through the ordinate to intercept the abscissa. The value of this intercept is the millilitres of $2{\cdot}0 \times 10^{-3}$M fluoride solution necessary to equal the apparent amount of fluoride present in the blank.

21.5.7.1 At the lower limits of the determination range, the response of the electrode may vary from a Nerstaan straight-line curve. Therefore, the readings obtained from the first few additions may vary from the straight line obtained from using the last four or five readings.

21.6 Procedure

21.6.1 Pipette an aliquot, generally 50 ml, of the sample into a 200-ml plastic beaker. While

stirring, add 4 drops of mixed indicator and acetic acid solution dropwise to a red end point (*p*H approximately 5·1). Add 50 ml of TISAB solution. If the volume of the solution is less than 100 ml, add water to dilute to 100 ml.

21.6.2 Follow procedure of **21.5.2** to **21.5.6.**

21.6.3 Determine the millilitres of 20×10^{-3} M fluoride solution necessary to equal the amount of fluoride in the sample by plotting the values obtained in step **21.6.1** and subtracting from this intercept value, the intercept value for the blank.

21.6.4 If the fluoride content of this solution is too large, the slope of the resultant curve, step **21.6.2** approaches zero. In this case, reduce the size of the sample aliquot.

21.7 Calculation

21.7.1 Calculate the parts per million of fluoride in the sample as follows:

$$I = I_s - I_b$$

$$\text{Fluoride, ppm} = I \times (2{\cdot}0 \times 10^{-3}) \times 18{\cdot}9984 \times \frac{1000 \text{ ml}}{V_1 \times S}$$

where

I_s = intercept value for sample;

I_b = intercept value for blank, $2{\cdot}0 \times 10^{-3}$

= molarity of working fluoride solution;

18·9984 = molecular weight of fluoride;

V_1 = aliquot size of sample taken in **21.5.7**, generally 50 ml, and

S = specific gravity of the sample.

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